Computational Nanotechnology of Materials, Electronics and Machines: Carbon Nanotubes

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IPT Integrated Product Team on Devices and Nanotechnology

The IPT vision is:

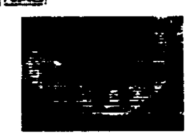
NASA Mission Needs

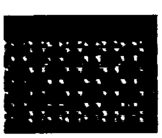
- Onboard computing systems for future autonomous intelligent vehicles
  - powerful
  - compact
  - low power consumption
  - radiation hard

- High performance computing (Tera- and Peta-flops)
  - processing satellite data
  - integrated space vehicle engineering
  - climate modeling
- Smart, compact sensors
- Light weight displays for space vehicles
- Advanced instrumentation for space astronomy

http://www.ipt.arc.nasa.gov/index.html

Research Focus





Techniques

- **Large Scale Classical Molecular Dynamics on a Shared Memory Architecture Machine**

  Tersoff-Brenner reactive many-body potential for hydrocarbons
  Long Range (6-12) Van der Walls interactions

  Parallel implementation on a shared memory Origin2000 machine

Srivastava and Barnard – **IEEE SuperComputing '97**

- **Quantum Molecular Dynamics Methodology**

  Tight-binding molecular dynamics in an non-orthogonal atomic basis (GTBMD) method.

  Previous Parametrization : Silicon and carbon
  M. Menon and K. R. subbaswamy, **Phys. Rev. B (1993-94)**

  Extended to heteroatomic systems including: C, B, N

  M. Menon and D. Srivastava,
  Chem. Phys. Lett. Vol. 307, 407 (1999)

Technique Development Focus I

Large Scale Classical Molecular Dynamics on a Shared Memory Architecture Machine

- Brenner's reactive many-body potential for hydrocarbons
  Long Range (6-12) Van der Walls interactions
- Parallel implementation on a shared memory Origin2000 machine
  - Cell method
  - Spatial Decomposition for Neighborlist
  - Lexical Decomposition for Force Calculations
    - better load balance

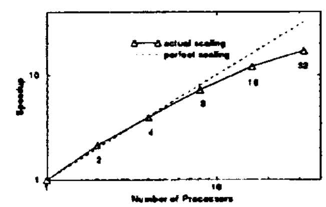


Figure 7: Scaling of the parallel Brenner's potential code on the SGI Origin2000, simulating compression of a four-wall carbon nanotube with 84400 atoms.

D. Srivastava and S. Barnard - IEEE SuperComputing '97 Proc.

Technique Development Focus II

Quantum Molecular Dynamics Methodology:

$$U = U_{el} + U_{rep} + U_0$$

$$U_{el} = \text{Sum [one electron energies]}$$

$$U_{rep} = \text{Sum [repulsive pair potential]}_{occupied}$$

- Non-othogonal atomic basis GTBMD method

Secular Eq. $\det\{ h_{ij} - E\, s_{ij} \} = 0$

The forces on an atomic coordinates are given by

$$F_x = - dU/dx$$

Molecular Dynamics : system is dynamically evolved at each time step

Previous Parametrization : Silicon and carbon
M. Menon and K. R. subbaswamy, Phys. Rev. B (1993-94)

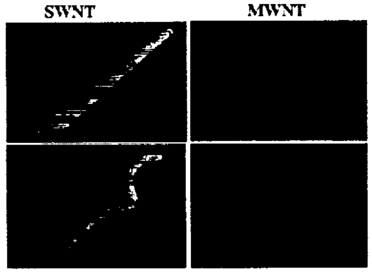
Extends to heteroatomic systems including: Si, C, B, N, and H

Research Focus I
Nanotube - Nanomechanics/materials

- Nanotubes are extremely strong highly elastic nanofibers
  - high value of Young modulus
    steel - 0.2 TPa
    swnt - 1.2 TPa
- **Dynamic response of nanotubes to ballistic deformation**
  - axial compression, bending and torsion
  - comparison between SWNT and MWNT behavior

(Axial Compression)

SWNT **MWNT**



- redistribution of strain, and side ways buckling

D. Srivastava et. al., Chapter 14, Vol 2, Handbook of Nanostructured Materials and Nanotechnology, Ed. H. S. Nalwa Academic Press, 2000

PHYSICAL REVIEW LETTERS

Nanomechanics of Carbon Tubes: Instabilities beyond Linear Response

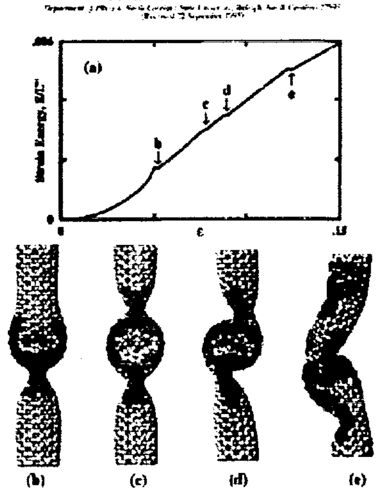
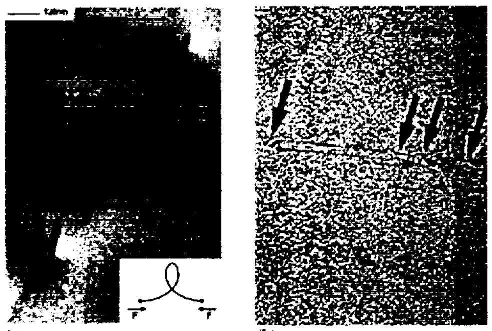


FIG. 1. MD-simulated nanotube of length $L = 6$ nm, diameter $d = 1$ nm, and armchair helicity (7,7) under axial compression. The strain energy (a) displays four singularities

Nanotubes in Composites

- Experiment : Buckling and Collapse of Embedded Carbon Nanotubes

O. Lourie et. al. Phys. Rev. Lett. Vol. 81, 1638 (1998).



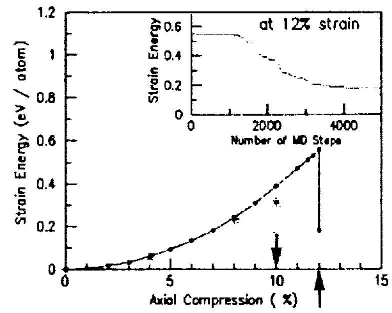
(a) (b)

Under Compressional strain two modes are observed

- (a) - long multi-wall nanotubes behave as elastic rods that buckle, bend and loop
- (b) - thin walled nanotubes locally collapse or fracture rather than buckle

Compressed Nanotubes in Composites

- Energetics of collapse-plasticity of (8,0) CNT at 12% compression strain.

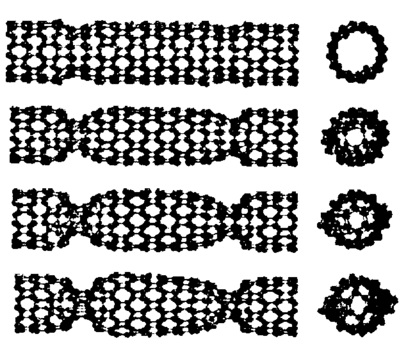


Quantum GTBMD Method
classical atomistic (with Tersoff-Brenner potential)

- Linear response regime (Y = 1.3 TPa) followed by pinching/buckling (classical MD) or collapse/plasticity (quantum MD).

Compressed Nanotubes in Composites

- Spontaneous collapse-plasticity of (8,0) CNT through graphitic (sp^2) to diamond like (sp^3) type transition.

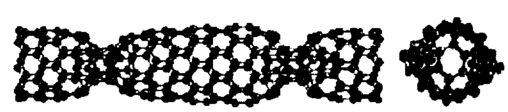


(a) side view (b) top view

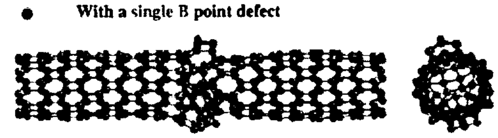
D. Srivastava, M. Menon and K. Cho, Phys. Rev. Lett. Vol. 83, 2973 (1999).

Compressed Nanotubes in Composites

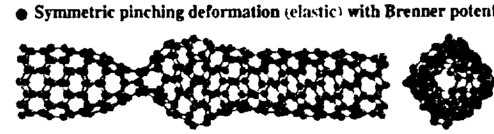
- Comparison with classical atomistic simulation, and a CNT with B point defect.



- With a single B point defect



- Symmetric pinching deformation (elastic) with Brenner potential



CxByNz Nanotubes

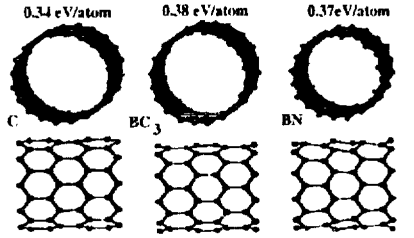
- **Band gap engineering over a larger range should be possible:**

BN	~ 5.5 eV
BC_2N	~ 2.0 eV
C	~ 0 – 1 eV
BC_3	~ 0.5 eV

  - a variety of junctions, quantum dots and superlattices should be possible
  - should be more robust

- **Example: Composite (10,0) nanotube**

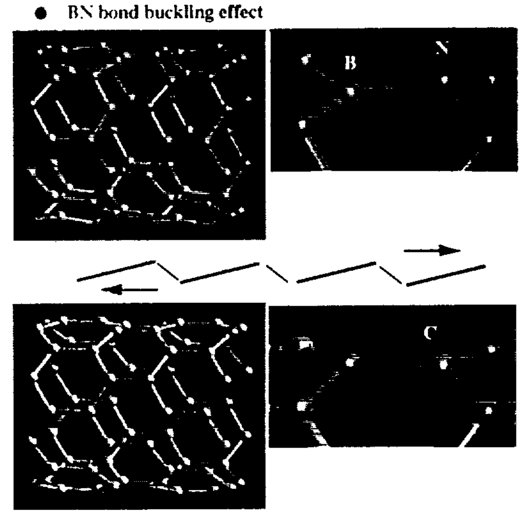
0.34 eV/atom 0.38 eV/atom 0.37eV/atom



reconstruction due to polar BN bond

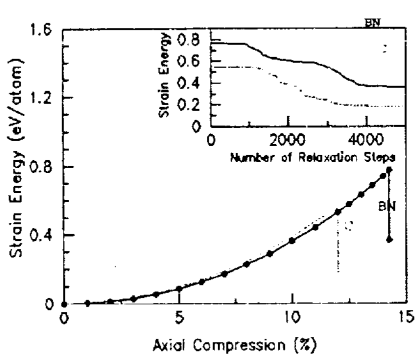
BN Nanotubes – Structure Simulations

- BN bond buckling effect

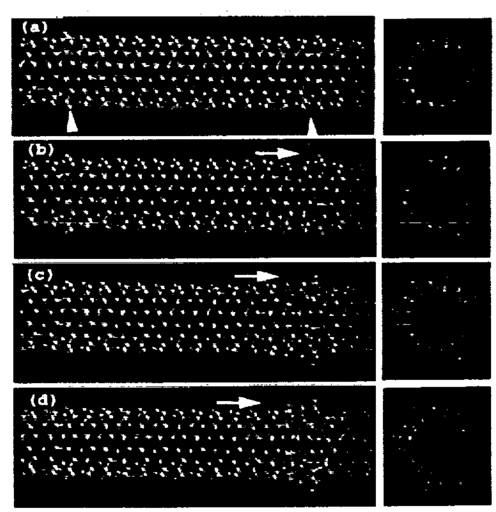


BN Nanotubes – Nanomechanics

- Young's modulus and plasticity of a compressed BN nanotube.



- Y (BN) = 1.2 TPa ~ BN is 92% as strong as CNT !
  Y (C) = 1.3 TPa
- BN nanotube plastically collapses at even higher strain than C nanotube.



Anisotropic Plastic Collapse of BN Nanotube

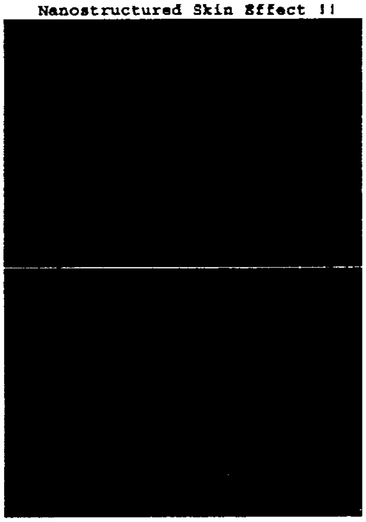
D. Srivastava, M. Menon and K. Cho, submitted (2000)

BN Nanotubes – Nanomechanics

Applications II

- **BN reinforce composites with anisotropic plasticity**

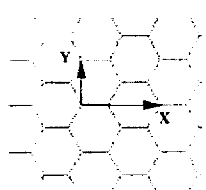
Nanostructured Skin Effect !!



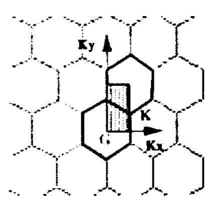
Carbon–based Electronics

- molecular wires
- topological defect mediated hetero–junctions ~ switching
  transisting
  tunneling devices
- C nanotubes doped with B and N
  BN nanotubes (insulator ~ 5eV gap)
  heterojunctions
  superlattices
- Combination of the above two ~ to taylor the probable device characteristics
- interconnects – Carbon/metal junctions

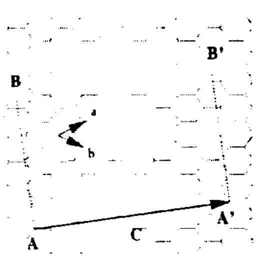
Carbon Nanotube Electronics Band Structure (basics)



Hexagonal Lattice of a Graphene Sheet – (2xunit cell)

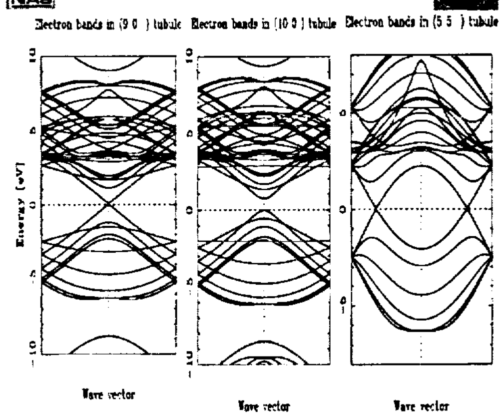


First Brillouin zone for an arm–chair tube



Ch = n a + m b (chiral vector)

Carbon Nanotube Electronics Band Structure



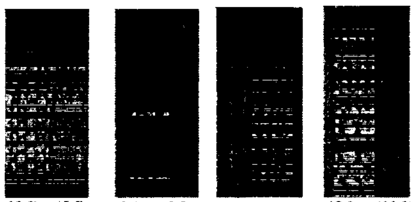
(9,0) tube (10,0) tube (5,5) tube

Arm chair tubes (n,n) ~ metal like

Otherwise m–n = 3l (l~ integer) metal like

Carbon based Electronics I

2- point Nanotube Heterojunctions
Molecular Electronic Switches



(10,0) – (6,6)   (9,0) – (5,5)   (8,0) – (7,1)   (12,0) – (11,0)

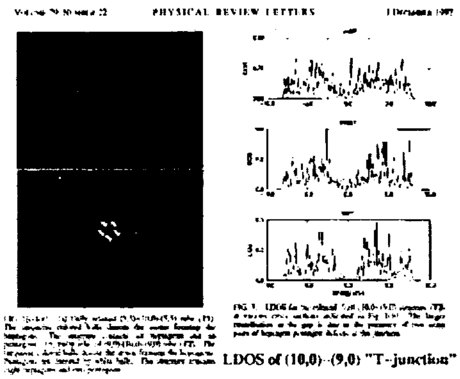
Bent Junctions   Straight Junctions

Semiconductor-Metal
Semimetal-Metal

Chico et. al. Phys. Rev. Lett., 96
Charlier et. al. Phys. Rev. B, 96
Lambine et. al. Chem. Phys. Lett., 96
Saito et. al. Phys. Rev. B, 96
M. Menon and D. Srivastava, J. Mat. Research, 98

We studied the effect of capping the tubes and relaxing the junctions with a quantum GTBMD method.

Carbon based Electronics II



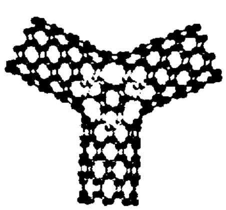
LDOS of (10,0)-(9,0) "T-junction"

3-terminal "T-tunnel" Junctions of Nanotubes

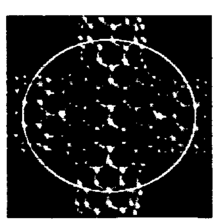
M. Menon and D. Srivastava, Phys. Rev. Lett. Vol 79, 4453 (1997)

Carbon based Electronics III

Pathways to Two Dimensional Molecular "Networks"



Metal-Semiconductor-Metal "Y" Tunnel Junction



A four-terminal nanotube heterojunction

M. Menon and D. Srivastava, Phys. Rev. Lett. (97)
D. Srivastava, S. Saini and M. Menon, Mol. Elec. Sci and Technol. (98)
M. Menon and D. Srivastava, J. Mater. Res. (98)

Research Focus III
BxCyNz Composite Nanotubes and Junctions

- **Band gap engineering over a larger range should be possible:**

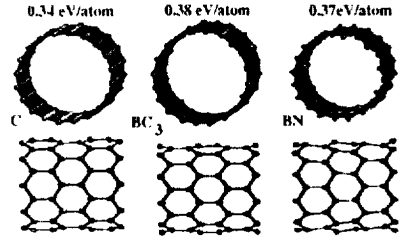
BN	~ 5.5 eV
BC_2N	~ 2.0 eV
C	~ 0 – 1 eV
BC_3	~ 0.5 eV

~ a variety of junctions, quantum dots and superlattices should be possible

~ should be more robust

- **Example: Composite (10,0) nanotube**

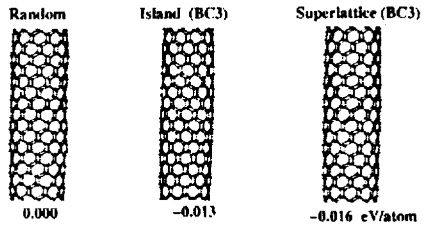
0.34 eV/atom   0.38 eV/atom   0.37eV/atom



reconstruction due to polar BN bond

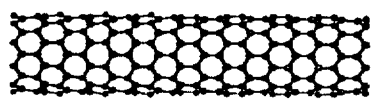
Composite Nanotubes and Junctions

- **B doping of Carbon Nanotube**



phase separation of doped and undoped regions is thermodynamically stable !

- **BN/C Junctions**

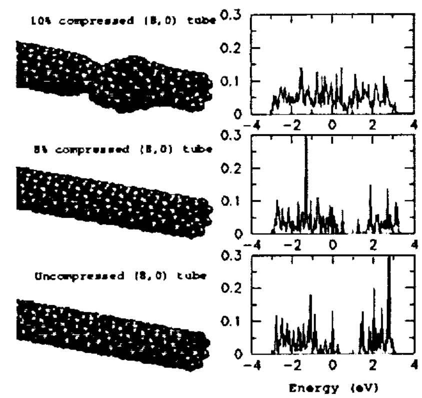


Interface Energy = 2*BN/C – BN – C
Interface Energy = 0.33eV/CB bond
Stable interfaces should be possible !

D. Srivastava and M. Menon, unpublished (1998)

Nano Mechano–Electronics I

- Mechanical deformations alter the Electronic Characteristics of Nanotubes

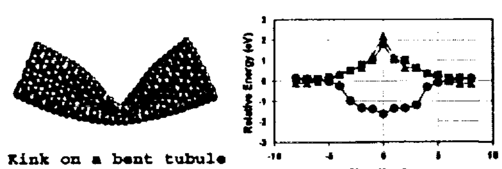


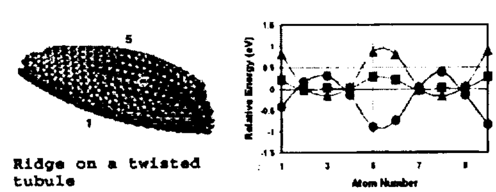
Nano mechano–electronics effects are "strongly" dependent on tube chiralities !

D. Srivastava and M. Menon, unpublished (1998)

Functionalization of Nanotubes Nano–Mechano–chemistry

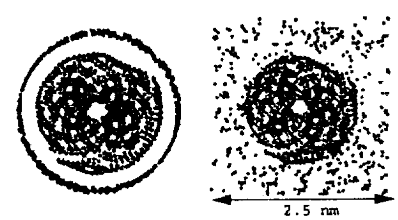
- Predictions of enhanced chemical reactivity in regions of local conformational strains: Kinky Chemistry

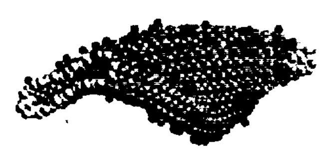




Binding Energy
Cohesive Energy
Electronic Energy

Functionalization of Nanotubes Nano–Mechano–Chemistry



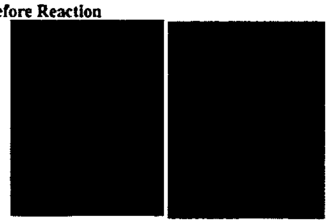


Torsionally twisted SWNT equilibrated in an H bath

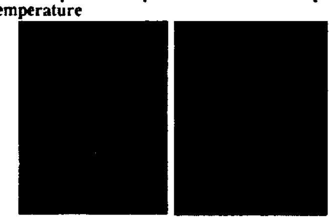
Nano Mechano–Chemistry

SEM images of MWNTs dispersed on a V–ridge substrate

(a) Before Reaction



(b) Same sample after exposure to nitric acid vapor at room temperature



"Predictions of enhanced chemical reactivity in regions of local conformational strains: kinky chemistry," D. Srivastava, J. D. Schall, D. W. Brenner, K. D. Ausman M. Feng, and R. Ruoff, J. Phys. Chem. Vol. 103, 4330 (99)

Comments:

Nanotechnology Materials and Applications.

- compressed C nanotubes in composites
- Nanostructured skin effect
  Functionality of a smart material
- Nano Electromechanical Sensors (NEMS)
- Components of Molecular Electronics
- mechanical kink catalyzed chemistry
  - kinky chemistry